Supplementary information for:

Insertion reactions of β-diketiminate-stabilised calcium amides with 1,3-dialkylcarbodiimides


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General Procedures

All manipulations were carried out using standard Schlenk line and glovebox techniques under an inert atmosphere of either nitrogen or argon. NMR experiments were conducted in Youngs tap NMR tubes made up and sealed in a Glovebox, NMR were collected on recorded either Bruker AV-500 spectrometer at (13C NMR 125.8 Hz) or a Bruker AV-400 spectrometer (13C NMR 100.6 MHz). Solvents (Toluene, Benzene, THF, Hexane) were dried by distillation from sodium-benzophenone ketyl, under nitrogen and stored in ampoules over molecular sieves. C6D6 and d8-toluene were purchased from Goss Scientific Instruments Ltd. and dried over molten potassium before distilling under nitrogen and storing over molecular sieves. (Tetrakis(trimethylsilyl))silane (TMSS) was purchased from Goss Scientific Instruments Ltd. and used as received. 1,3-Dialkylcarbodiimides were purchased from Sigma-Aldrich and used as received. The β-diketiminate ligand, and heteroleptic calcium amides 1-4 were synthesised by literature procedures.2-3
NMR Scales reactions

In a glovebox the β-diketiminate stabilised calcium amide (2-4, 0.05 mmol) was dissolved in C₆D₆, the 1,3-dialkylcarbodiimide (0.05 mmol) was added via micropipette (or as a solid) and the solution was transferred to a Youngs tap NMR tube. The reaction was monitored by ¹H and ¹³C NMR spectroscopy. In situ ¹H NMR data (C₆D₆, 298 K, 400 MHz) 5: 0.97 (d, 12H, J = 6.2 Hz), 1.31 (d, 12H, J = 6.8 Hz), 1.32 (d, 12H, J = 6.8 Hz), 1.39 (d, 12H, J = 6.9 Hz), 1.77 (s, 6H), 3.49 (hept, 4H, J = 6.8 Hz), 3.55 (hept, 2H, J = 6.2 Hz), 3.73 (hept, 2H, J = 6.9 Hz), 4.88 (s, 1H), 5.22 (s, 1H), 7.13-7.20 (m, 9H).

Figure 1. NMR scale reaction between 2 and 1,3-diisopropylcarbodiimide. Top (isolated compound 2), bottom (30 min after addition of a 1,3-diisopropylcarbodiimide).
Synthesis of heteroleptic guanidinate complexes

6: To a solution of \([\{\text{ArNC(Me)CHC(Me)NAr}\}_2\text{Ca(NHAr)}(\text{THF})]\) (2, 600 mg, 0.87 mmol) in hexane was added 1,3-dicyclohexylcarbodiimide (178 mg, 0.86 mmol) as a solution in the same solvent. The solution was stirred for 1 h at room temperature, filtered and the volume reduced to induce crystallization. 6 was isolated as a colourless crystalline solid (mg, mmol, %) yield by $^1$H NMR. $^1$H NMR (C$_6$D$_6$, 298K, 400 MHz) 0.98-1.07 (m, 9H), 1.15 (m, 4H, THF), 1.29 (d, 12H, $J$ = 6.9 Hz), 1.33 (d, 12H, $J$ = 6.8 Hz), 1.40 (d, 12H, $J$ = 6.8 Hz), 1.49-1.52 (m, 3H), 1.61-1.66 (m, 8H), 1.70 (s, 6H), 2.98-3.03 (m, 2H), 3.33 (m, 4H, THF), 3.47 (hept, 4H, $J$ = 6.8 Hz), 3.67 (m, 12H, $J$ = 6.9 Hz), 4.91 (s, 1H), 5.26 (broad s, 1H), 7.10-7.21 (m, 9H); $^{13}$C NMR (C$_6$D$_6$, 298K, 125.8 MHz) 25.1, 25.2, 25.4, 26.5, 26.6, 28.3, 28.3, 28.5, 37.7, 54.8, 68.3, 93.5, 123.2, 123.6, 123.7, 124.0, 138.9, 141.6, 144.9, 148.4, 160.3, 165.4. Anal. Calc. for C$_{58}$H$_{89}$CaN$_5$O: C 76.28 H 9.75 N 7.67. Found: C..H..N.

7: To a solution of \([\{\text{ArNC(Me)CHC(Me)NAr}\}_2\text{Ca(NPh$_2$)}(\text{THF})]\) (3, 516 mg, 0.74 mmol) in hexane was added 1,3-dicyclohexylcarbodiimide (154 mg, 0.74 mmol) as a solution in the same solvent. The solution was stirred for 1 h at room temperature, filtered and the volume reduced to induce crystallization. 7 was isolated as a colourless crystalline solid (148 mg, 0.164 mmol, 22 %). $^1$H NMR (C$_6$D$_6$, 298K, 500 MHz) 0.80-1.02 (m, 5H), 1.08-1.21 (m, 7H), 1.13 (m, 4H, THF), 1.24 (d, 12H, $J$ = 6.8 Hz), 1.38 (d, 12H, $J$ = 6.8 Hz), 1.48-1.58 (m, 8H), 1.77 (s, 6H), 3.34 (m, 2H), 3.36 (hept, 4H, $J$ = 6.8 Hz), 3.48 (m, 4H, THF), 4.95 (s, 1H), 6.86 (t, 2H, $J$ = 7.0 Hz), 7.10-7.23 (m, 10H), 7.38 (d, 4H, $J$ = 8.0 Hz); $^{13}$C NMR (C$_6$D$_6$, 298K, 125.8 MHz) 24.7, 25.2, 25.5, 25.9, 26.3, 26.6, 28.5, 37.1, 56.0, 68.8, 94.1, 120.7, 121.5, 123.9, 124.2, 129.2, 141.5, 146.2, 148.5, 163.0, 165.7. Anal. Calc. for C$_{58}$H$_{81}$CaN$_5$O: C 76.96 H 8.96 N 7.74. Found: C..H..N.

8·THF: A solution of 2-methoxyethylamine (67 mg, 0.89 mmol), and 1,3-diisopropylcarbodiimide (112 mg, 0.89 mmol) in hexane (10 mL) were added to a
solution of 1 (600 mg, 0.89 mmol) in the same solvent (20 mL). The reaction was stirred for 1 h at room temperature, filtered and the solvent volume reduced to ca 10 mL. The product crystallised upon storage of this solution at -21°C for 24h, and isolation by filtration gave 8·THF (230 mg, 0.32 mmol, 35 %) as a colourless crystalline solid. \(^1\)H NMR (C\(_6\)D\(_6\), 353K, 400 MHz) 1.02 (d, 6H, \(J = 6.0\) Hz), 1.05 (d, 6H, \(J = 6.1\) Hz), 1.29 (d, 12H, \(J = 6.8\) Hz), 1.31 (d, 12H, \(J = 6.8\) Hz), 1.50-1.54 (m, 4H), 1.75 (s, 6H), 2.91 (s, 3H), 3.10-3.16 (m, 4H), 3.20 (hept, 2H, \(J = 6.1\) Hz), 3.34 (hept, 4H, \(J = 6.8\) Hz), 3.41 (broad s, 1H), 3.43 (hept, 2H, \(J = 6.0\) Hz), 3.55-3.58 (m, 4H), 4.82 (s, 1H), 7.00-7.15 (m, 6H); \(^13\)C NMR (C\(_6\)D\(_6\), 298K, 125.8 MHz) 20.9, 23.5, 24.0, 24.6, 25.2, 25.8, 26.7, 28.3, 28.6, 44.5, 46.6, 47.8, 58.5, 67.8, 76.9, 91.7, 94.2, 124.0, 123.6, 141.5, 147.4, 165.2, 165.7. Anal. Calc. for C\(_{43}\)H\(_{71}\)CaN\(_5\)O\(_2\): C 70.67 H 9.72 N 9.59. Found: C...H...N.

References


NMR data for compounds 6,7 (C₆D₆, 298K) and 8·THF (d₈-toluene, 298K)